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Procedia Engineering 44 (2012) 269 – 272

Procedia Engineering

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Euromembrane Conference 2012

[OB33]

Removal mechanisms of trace organic contaminants in osmotically driven membrane process

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In this study, we characterised the properties (surface charge, hydrophobicity, reverse salt flux, permeability and pore radius) of a commercially available cellulose-based FO membrane to facilitate the understanding of the transport of trace organic contaminants (TrOCs) in an osmotically driven process. We then systematically investigated and compared removal behaviours of TrOCs in RO and FO modes using varying types of draw solutes. Furthermore, humic acid fouling and its associated effect on the removal of TrOCs were explored. We thereby propose and delineate the impact of reverse solute transport on the removal of TrOCs in both clean and humic acid fouling matrixes by the FO process.

The average membrane pore radius was determined from retention data of inert organic reference solutes (i.e., erythritol, xylose and glucose) and the membrane pore transport model. Filtration experiments in the FO and RO modes where the membrane active layer faces to the feed solution were conducted in lab-scale flat-sheet crossflow setups. Five representative TrOCs, namely carbamazepine, sulfamethoxazole, bisphenol A, triclosan and diclofenac were employed to demonstrate various solute-membrane interactions in FO.

Different removal behaviour of TrOCs was observed in the FO and RO modes. When NaCl was used as the draw solute, the removal of all five TrOCs in the FO mode was consistently higher than that in the RO mode at the same water permeate flux of 5.4 L/m^{2}h. At the same time, the adsorption amount of three hydrophobic TrOCs (bisphenol A, triclosan and diclofenac) to the membrane in the FO mode was consistently lower than that in the RO mode. Given that the molecular dimension of these TrOCs are comparable or larger than the calculated mean effective membrane pore radius of 0.37 nm, we hypothesized that the forward diffusion of TrOCs were retarded by the high reverse salt flux of 4.28 g/m^{2}h induced by 0.5 M NaCl draw solution within the membrane pore in the FO mode. This retarded forward diffusion of TrOCs by high reverse solute flux leads to a higher removal in the FO mode than that in the RO mode. We further verified the retarded forward diffusion effect by using draw solute with low reverse solute flux (Figure 1). When glucose (3 M) and $MgSO_4$ (2.5 M) were used as draw solutes to induce a water flux of 5.4 L/m^{2}h which can be obtained with a draw solution of 0.5 M NaCl, the removal and adsorption amount of bisphenol A in the FO mode were similar to those in the RO mode.

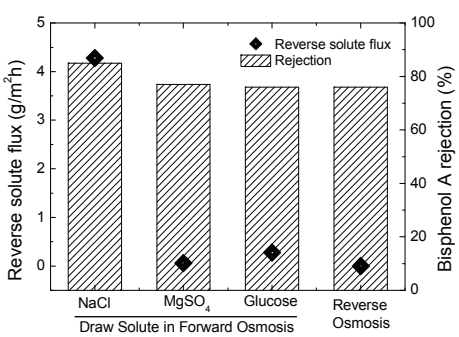

Figure 1: BPA rejection and reverse solute flux in the FO mode using 0.5 M NaCl, 2.5 M $MgSO_4$ and 3 M glucose as draw solute to induce the same permeate water flux of 5.4 L/m^{2}h. The FO experimental conditions were as follows: the initial concentration of BPA in the feed = 500 µg/L,

doi:10.1016/j.proeng.2012.08.383

pH = 7, the background electrolyte contained 20 mM NaCl and 1 mM $NaHCO_3$, crossflow rate = 1 L/min for both sides (corresponding to the crossflow velocity of 9 cm/s). The temperature of feed and draw solution was 25±1 °C.

In the presence of a humic acid cake layer on the membrane surface, the removal of carbamazepine and sulfamethoxazole increased from 80 to 89% and 83 to 96%, respectively, in the FO mode using 0.5 M NaCl as draw solute at the same initial water flux (Figure 2). The increased removal of carbamazepine and sulfamethoxazole simultaneously with the reduced reverse salt flux in the FO mode suggested that the humic acid fouling layer act as an additional filtration barrier.

Reverse solute flux plays an important role in the removal of TrOCs in the humic acid fouled FO membrane (Figure 2). We compared the removal of carbamazepine and sulfamethoxazole using $MgSO_4$ (2.5 M) and glucose (3 M) to that using NaCl (0.5 M) at the same initial water flux (Figure 3) in presence of a humic acid cake layer on the membrane surface. The removal of carbamazepine decreased from 89 to 84% and that of sulfamethoxazole reduced from 99 to 94 % when these two draw solutes with low reverse solute flux were used (Table 1). Moreover, there was negligible difference in the removal of carbamazepine and sulfamethoxazole using draw solutes with low reverse solute flux. It was noteworthy that the deposited amount of humic acid and reverse solute flux using NaCl (0.5 M) was twice and tenfold higher than that using $MgSO_4$ (2.5 M) and glucose (3 M) as the draw solute, respectively (Table 1). Draw solute with high reverse solute flux leads to an elevated ionic strength at the membrane surface, which favoured the deposit of humic acid. Therefore, the humic acid fouling layer acted as an additional filtration barrier and blocked the reverse transport of draw solute. This additional filtration barrier lead to a higher TrOCs removal in humic acid fouling matrix compared to that in the clean feed matrix, and the removal of TrOCs in the humic acid fouling matrix was lower when draw solutes with low reverse solute flux (e.g., $MgSO_4$ and glucose) were employed than that when draw solute with high reverse solute flux (e.g., NaCl).

Table 1: Reverse NaCl flux and humic acid deposit amount in the humic acid fouling in FO. The standard deviation was calculated from the results of duplicate experiments.

Experimental condition			Reverse solute flux	Humic acid deposit
Feed pH	Feed matrix	Draw solute	g/(m^2h)	(mg/cm^2)
6.5	Clean[1]	0.5 M NaCl	3.51 ± 0.02	N.A.
		2.5 M $MgSO_4$	0.21	
		3 M Glucose	0.25	
	Fouled[2]	0.5 M NaCl	1.38 ± 0.05	4.64 ± 0.78
		2.5 M $MgSO_4$	0.18 ± 0.35	2.37 ± 0.53
		3 M Glucose	0.13	2.24

[1] Clean feed matrix contains 500 µg/L carbamazepine and sulfamethoxazole in the background electrolyte solution (20 mM NaCl and 1 mM $NaHCO_3$)

[2] Fouling feed matrix contains 500 µg/L carbamazepine and sulfamethoxazole, 50 mg/L humic acid and 2 mM Ca^{2+} in the background electrolyte solution (20 mM NaCl and 1 mM $NaHCO_3$)

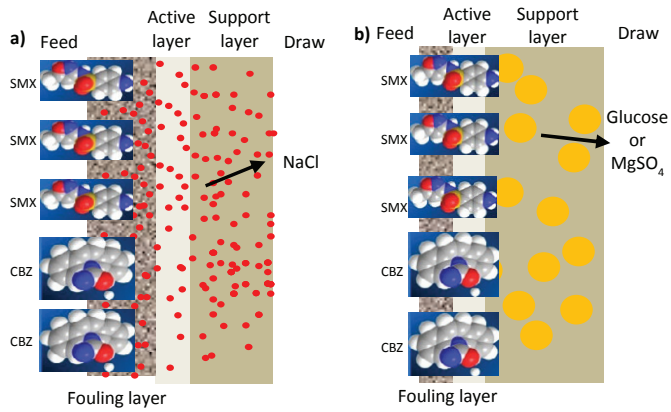

Figure 2: Conceptual illustration of the impact of reverse draw solute on TrOCs removal in the humic acid fouling by FO process using **a)** high reverse transport draw solute and **b)** low reverse transport draw solute. SMX = sulfamethoxazole and CBZ = carbamazepine.

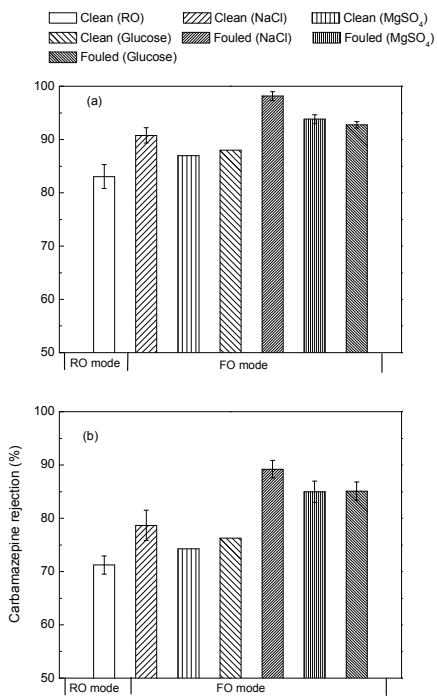

Figure 3: Comparison of rejections of (a) sulfamethoxazole and (b) carbamazepine in the RO and FO modes. The FO experimental conditions were as follows: the initial concentrations of sulfamethoxazole and carbamazepine in the feed = 500 µg/L, initial feed pH = 6.5, initial humic acid concentration (fouling condition) = 50 mg/L, the background electrolyte solution contained 20 mM NaCl, 1 mM $NaHCO_3$ and 2 mM Ca^{2+}. Varying draw solutions were 0.5 M NaCl, 2.5 M $MgSO_4$ and 3 M glucose. The feed and draw solution temperatures were 25±1 °C. Crossflow rate = 1 L/min for both sides (corresponding to the crossflow velocity of 9 cm/s). RO experimental conditions were as follow: the initial concentrations of sulfamethoxazole and carbamazepine in the feed = 500 µg/L, initial feed pH = 6.5, the background electrolyte solution

contained 20 mM NaCl, 1 mM $NaHCO_3$ and 2 mM Ca^{2+}. Operating pressure = 10 bar, crossflow rate = 1 L/min (corresponding to the crossflow velocity of 25 cm/s), feed solution temperature = 25±1 °C. Error bar represents the standard deviation calculated from duplicate experiments.

Keywords: Forward osmosis, Trace organic contaminant, Removal mechanism, Retarded foward diffusion